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Hydrocarbons in Sediments and Benthic Organisms from a Dredge Spoil Disposal Site in RI Sound

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Prepared for

Environmental Research Lab, Narragansett, R I

Nov 77

PB 276 732

EPA-600/3-77-092
November 1977

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-77-092		PB276732

4. TITLE AND SUBTITLE
Hydrocarbons in Sediments and Benthic Organisms from a Dredge Spoil Disposal Site in RI Sound

5. REPORT DATE
November 1977 issuing date

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Paul D. Boehm and James G. Quinn

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Graduate School of Oceanography
University of Rhode Island
Kingston, Rhode Island 02881

10. PROGRAM ELEMENT NO.
1BA608

11. CONTRACT/GRANT NO.
R803415

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Research Laboratory - Narragansett, RI
Office of Research and Development
U.S. Environmental Protection Agency
Narragansett, Rhode Island 02882

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA/600/05

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Geochemistry Hydrocarbons	Hydrocarbon pollution Dredge spoil Bioaccumulation	08/A 08/D 08/H

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	49
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE A03 - A01

EPA Form 2220-1 (9-73)

* U.S. GOVERNMENT PRINTING OFFICE: 1978—757-140/6616

EPA-600/3-77-092
November 1977

HYDROCARBONS IN SEDIMENTS AND BENTHIC ORGANISMS FROM A DREDGE SPOIL DISPOSAL SITE IN RHODE ISLAND SOUND

by

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FOREWORD

The Environmental Research Laboratory of the U.S. Environmental Protection Agency is located on the shore of Narragansett Bay, Rhode Island. In order to assure the protection of marine resources, the laboratory is charged with providing a scientifically sound basis for Agency decisions on the environmental safety of various uses of marine systems. To a great extent, this requires research on the tolerance of marine organisms and their life stages as well as of ecosystems to many forms of pollution stress. In addition, a knowledge of pollutant transport and fate is needed.

This report describes a three-year study to investigate the spatial distribution of hydrocarbons both in surface sediments from upper Rhode Island Sound and in a commercially important shellfish from the area, the ocean quahog (Acartia islandica). An attempt is made to distinguish the regular hydrocarbon geochemistry of Rhode Island Sound, defined by background hydrocarbon distributions and inputs from Narragansett Bay and adjacent coastal areas, from the input due to mobilization of hydrocarbons from a deposited dredge spoil during the five years since the disposal activity has ceased.

ABSTRACT

The hydrocarbon contents of surface sediments, sediment cores, and ocean quahogs (Arctica islandica) from Rhode Island Sound have been determined. Hydrocarbon concentrations in surface sediments normally range from 1.0 to 56.1 μg/g, largely dependent on sediment type and sedimentation rates. However, concentrations up to 301 μg/g are observed in surface samples from a dredge spoil deposit located in the study area. Based on 1) qualitative and quantitative hydrocarbon distributions in the sediments, 2) the hydrocarbon to organic carbon ratio, and 3) the ratio of the concentration of a prominent cycloalkene compound to organic carbon, the normal hydrocarbon geochemistry of the region is defined. Using these criteria, the effect of the dredge spoil deposit (containing 5 to 20 x 10^3 metric tons of hydrocarbons) is seen to be insignificant beyond 2 km from the disposal site.

Hydrocarbon contents of the ocean quahog do not reflect the sediment distributions qualitatively or quantitatively. Throughout the study area the clams' hydrocarbon contents vary by a factor of 2.5 (2.6 to 6.4 μg/g wet) while the sediment concentrations vary by two orders of magnitude. The hydrocarbon assemblage in the clams exhibits a lower boiling point distribution than that in the sediments.

Key components of the surface sediments are two cycloalkene compounds of molecular weight 344 and 348. Their concentration covaries very significantly with the organic carbon content of the sediment. A major component of Arctica is another related cycloalkene of molecular weight 342. This compound is not present in the sediment.

A sediment core from the area shows a decreasing concentration of hydrocarbons and a decreasing percentage of unresolved components (UCM) with increasing depth. It is proposed that the rapid increase in the quantity of the UCM observed at a certain depth within the sediment, can serve as a chemical marker in the recent sedimentary record. This marker corresponds to the onset of the industrial revolution and the increased usage of petroleum products.

This report was submitted in fulfillment of Grant Number R803415 under the sponsorship of the Environmental Protection Agency. The work cited in this report was completed as of January 1977 and is included in the Ph.D. thesis of Paul D. Boehm (University of Rhode Island, 1977). This work has also been submitted (March, 1977) for publication to the Journal, Estuarine and Coastal Marine Science in a paper entitled, "Benthic Hydrocarbons of Rhode Island Sound," by Paul D. Boehm and James G. Quinn.

CONTENTS

	Page
Foreword	iii
Abstract	iv
List of Figures	vi
List of Tables	vii
Acknowledgements	viii
I. Introduction	1
II. Methods and Materials	5
III. Results	9
IV. Discussion	28
V. References	35

FIGURES

No.		Page
1.	Location of study area with sampling station numbers and sediment types	3
2.	Representative gas chromatograms of R. I. Sound *Arctica islandica* specimens (a); R. I. Sound surface sediment (b); Providence River surface sediment adjacent to sewage outfall (c)	12
3.	Mass spectra of unknown compounds	14
4.	Relation of organic carbon content of sediment to concentration of compound Y (HC 344) in sediment	16
5.	Relation of organic carbon content of sediment to its total hydrocarbon content	18
6.	Gas chromatograms of hydrocarbons in sediment core from station 17	20
7.	Gas chromatograms of hydrocarbons in sediment core from station 4	21

TABLES

No.		Page
1.	Hydrocarbon content of Rhode Island Sound surface sediments.	10
2.	Relevant data on cycloalkene compounds.	15
3.	Hydrocarbon concentrations relative to organic carbon contents of R. I. Sound and Narragansett Bay sediments.	19
4.	Hydrocarbon content of Rhode Island Sound sediment cores.	22
5.	Hydrocarbon concentrations in *Arctica islandica* of Rhode Island Sound.	25
6.	*Arctica* hydrocarbon intercalibration study.	27

ACKNOWLEDGMENTS

We would like to express our appreciation to the following individuals who contributed to the various analytical aspects of this study: Dr. Chris Brown (URI), Infrared spectra; Dr. Michael Missakian (URI), NMR spectra; Dr. Nelson Frew (WHOI), Curt Norwood (EPA), GC/MS spectra; Andy Sweatt (URI), Organic carbon analyses. Dr. Gerry Pesch and Bruce Reynolds (EPA, Narragansett) aided with the sampling and all shipboard activities, as did Don Wilcox, the skipper of the Hazel II. We also thank Sheldon Pratt (URI) for his expert advice on the benthic biology of Rhode Island Sound. We also appreciate the comments of Dr. John Farrington (WHOI) on the content of this manuscript. Finally, we wish to thank Anthony Paulson (URI) with whom we had useful discussions on the potential significance of the PCB-hydrocarbon relationship in sediment cores.

SECTION I

INTRODUCTION

Rhode Island Sound is that region of coastal water separating Narragansett Bay from the open waters of the Atlantic Ocean. It is bounded on the west by Block Island Sound and on the east by Buzzards Bay and Vineyard Sound (Fig. 1). Between December 1967 and September 1970, R. I. Sound received 6.3×10^6 cubic meters of dredge spoil originating in the Providence River, which flows into the Narragansett Bay estuary south of the city of Providence (Saila et al., 1972). Coming from an area of considerable shipping activity and municipal sewage input, the dredge spoil contained large amounts of associated anthropogenic hydrocarbons (Schultz, 1974; Farrington and Quinn, 1973a, b). This spoil was dumped in a 1.9 kilometer square disposal site located approximately 6.5 kilometers south of Newport, R. I. (Fig. 1).

It is the purpose of this study to investigate the spatial distribution of hydrocarbons both in upper R. I. Sound surface sediments and in the commercially important shellfish from the area, the ocean quahog (Arctica islandica). In doing so, we attempt to distinguish the regular hydrocarbon geochemistry of R. I. Sound, defined by background hydrocarbon distributions and inputs from Narragansett Bay and adjacent coastal areas, from the input due to mobilization of hydrocarbons from the deposited dredge spoil during the five years since the disposal activity has ceased.

GENERAL DESCRIPTION OF STUDY AREA

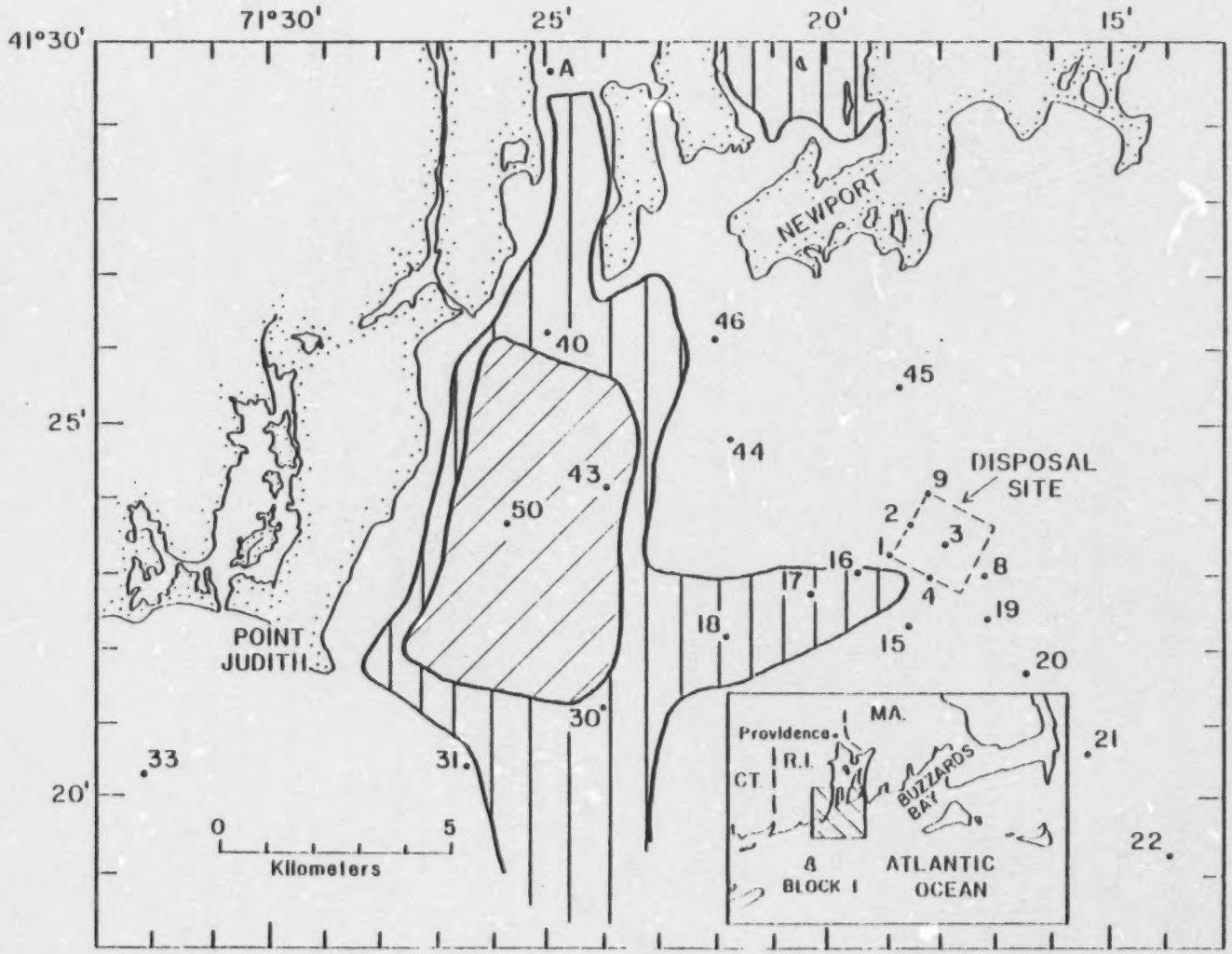
Physical Circulation

An investigation of the current systems in R. I. Sound (Shonting, 1969) indicated that while the upper layer motion is characterized by a net westward migrating drift and bottom motions by anticyclonic swirls with small net displacement, the currents in this region are dominated by the semidiurnal tide. The net transport of water due to the semidiurnal tide is small and neither the net tidal transport velocity nor the magnitude of the instantaneous bottom current are effective in resuspending sediment (0.1 and 0.3 knots respectively) (Saila et al., 1972).

Wave induced orbital motion of bottom waters at a depth of 30 meters can exceed that velocity ($\sim$0.3 knots = 15 cm/sec) theoretically necessary to resuspend normally deposited unconsolidated sediments in the 0.1 to 1.0 mm size range, especially during winter months. However, Saila et al. (1972) concluded that while resuspension activity by waves should be

Figure 1. Location of study area with sampling station numbers and sediment types.

Sediment types:


71°30'
25'
20'
15'
41°30'
25'
20'
A
NEWPORT
40
46
45
44
43
50
DISPOSAL SITE
9
2
3
1
16
8
17
4
19
18
15
20
POINT JUDITH
30
33
31
21
22
0
5
Kilometers
Providence
MA.
R.I.
CT.
BUZZARDS BAY
BLOCK I
ATLANTIC OCEAN

important at the depth of the dump site (27-30.5 meters), the mode of deposition of the spoil, plus its mechanical characteristics, have created an erosion resistant deposition consisting of sediment that can not be considered unconsolidated.

Sediment Characteristics of R. I. Sound

An extensive survey of R. I. Sound surface sediments by McMaster (1960) revealed that the study area as shown in Figure 1 consisted of well sorted fine sand. A large area of silty sand occurs adjacent to the R. I. mainland and a tongue of this finer sediment lies adjacent to the disposal site on the southwest. A core of sandy silt is found south of the West Passage of Narragansett Bay and adjacent to the mainland. McMaster's study indicates that clay sized particles do not accumulate in this area, indicating that the finer sediment, presumably of higher organic content, is transported farther out to sea. In general the quantity of sediment available for deposition in R. I. Sound is small and storm surges which resuspend unconsolidated sediment in the Narragansett Bay/R. I. Sound system probably play significant roles in defining sediment character and accumulation rates (Collins, 1976). The silt deposited in the settling basin adjacent to the mainland is probably transported out of the Bay south and westward by near surface currents with coarser silt settling east of the mainland and finer materials being transported around Pt. Judith into Block Island Sound (Collins, 1976).

Dredge Spoil Disposal

During the 34 month period when the dredging of the Providence River navigation channel took place, disposal of mud of high organic content ($\sim$4% organic carbon; Farrington and Quinn, 1973a) was followed by disposal of material of lower organic content. Thus silty sediment containing roughly 1-6 mg hydrocarbon/g (Farrington and Quinn, 1973a, Van Vleet and Quinn, 1977) was buried by silt and sand of lower organic content ($\sim$1% organic carbon) and lower hydrocarbon content. A large volume of the spoil consisted of compact material deposited prior to the time when man first significantly affected the estuary (Saila et al., 1972) and most likely consisted of 0.01-0.05 mg hydrocarbons/gram. The resulting 5.5 meter high mound of spoil deposited in the Sound at a water depth of 29.5-30.5 meters has a diameter of approximately 1.6 kilometers.

Based on the above we estimate that within this mound lies 5-20 x 10^3 metric tons of hydrocarbons. The post depositional fate of these hydrocarbons is the focus of this study.

SECTION II

METHODS AND MATERIALS

SAMPLING

Throughout the sampling program special precautions were taken to avoid any contamination from sampling and storage containers. Surface sediment samples at 21 stations in the study area were obtained on two cruises dating 6/27/75 and 7/7/75. A Smith-MacIntyre grab sampler obtained a relatively undisturbed 0.25 m^2, 10 cm deep sediment sample which when brought on board was subsampled randomly throughout the sample with a stainless steel trowel. In this manner approximately 500 g (wet weight) of sediment were obtained and stored in solvent prerinsed glass jars with aluminum foil-lined caps and were frozen at -20°C approximately 6 hours later. Two replicate grab samples were taken at each station, and subsampling duplicates of each grab were obtained, making a total of 4 samples for analysis from each station.

Sediment cores were obtained at stations 4 and 17 as they represented stations inside and outside of the disposal area respectively. Cores of approximately 40 cm length were obtained using a gravity corer with 60 kg of weight. The plastic core liners containing the sediment were frozen at -20°C until subsampling was performed. When cut into sections the sediment which had come in contact with the core liner was shaved off and discarded.

Ocean quahog specimens were collected on three different sampling dates, 3/6/75, 6/27/75, 7/7/75 from many of the stations shown in Figure 1. Benthic quahog sampling stations were coincident with surface sediment stations except where animals were absent or in low abundance due to natural population variations in the area. Sampling was accomplished using a rocking chair dredge. The animals were placed in plastic bags and chilled over ice on board and then frozen back in the laboratory at -20°C until analyzed.

Navigation was accomplished using Loran C which is accurate to within 200 meters in this region.

ANALYTICAL METHODS

Extractions

Sediment and sediment cores--

Samples were thawed overnight and then wet sieved by slurrying with distilled water, sieving through a 1 mm stainless steel screen and vacuum filtering through a Whatman 90 filter. Analysis of the filtrate showed that negligible quantities of hydrocarbons are lost by wet sieving in distilled water; i.e. these compounds remain associated with the sediments. Wet sieving removes both shell fragments and any macrofauna and also insures a relatively homogeneous sample from which one or two subsamples of approximately 50 grams wet weight each were obtained for analysis. A 10 gram subsample was transferred to a tared beaker and dried at 100°C for 4 hours to obtain moisture content.

Methods of extracting hydrocarbons from sediments are discussed by Farrington and Tripp (1975), and Rohrback and Reed (1975).

The extraction method chosen was a simultaneous saponification-extraction technique using 0.5 N KOH in anhydrous methanol, benzene and distilled water in volume ratios of 2:1:0.2 and using 500 ml of total solvent to extract a 50 gram wet weight sediment sample. This procedure both extracts and saponifies the sample in one step. Samples with 50 μg n-C_{20} (eicosane) added as an internal standard were extracted under reflux for 2 hours in a 1 liter round bottom flask.

Doubling the extraction time had no effect on the extraction efficiency. Re-refluxing the sediment residue from a 2-hour extraction for an additional 2 hours with fresh solvent yielded less than 1% additional hydrocarbon material.

After extraction, the mixture was filtered through a preignited (4 hrs at 450°C) Whatman GF/C filter and the residue extensively rinsed with petroleum ether. The extraction mixture was combined with the rinses and 100 ml distilled water added. The benzene-petroleum ether phase (non-saponifiable fraction) was isolated and the methanol-water phase extracted twice with 100 ml portions of petroleum ether. The combined benzene and petroleum ether extracts were combined and taken to dryness on a rotary flash evaporator at 30°C or less.

Arctica islandica--

Approximately 200 grams (2-3 animals) of tissues and fluids were removed from thawed specimens and homogenized in a Waring Blendor. To the homogenate (~90% water) was added 50 μg n-C_{20} internal standard, 250 ml of benzene and 100 ml 0.5 N KOH/methanol. The saponification-extraction proceeded under reflux for 2 hours whereupon the benzene layer was decanted. We examined the effect of changing the solvent ratios, saponifying for 2 hours with 0.5 N KOH/MeOH followed by benzene extraction, doubling the refluxing time, and doubling the normality of KOH and found no significant changes in the quantities of hydrocarbons extracted. We did

find, however, that a methanol-benzene extraction under reflux was only, on the average, 50% as efficient as was the saponification-extraction which digests the tissues. This result is most likely due to insufficient homogenation using the blender. Farrington and Medeiros (1975) employed a high speed Virtis homogenizer and found the extraction method applied to their homogenate to be less critical than our large discrepancy would imply.

The extracted non-saponifiable compounds in the benzene phase were taken to dryness on a rotary flash evaporator.

Chromatographic Procedures

Due to the large amount of pigment material extracted from the sediments in the nonsaponifiable fraction, an initial cleanup procedure was employed prior to thin layer chromatographic (TLC) separation. This involved charging the residue from the above sediment extract in a small volume of petroleum ether:benzene (95:5) to a 6 mm i.d. column containing 1 gram of alumina deactivated with 5% water. Using 5 bed volumes (~5 ml) of this 95:5 mixture was sufficient to elute both aliphatic, olefinic and aromatic hydrocarbons while leaving most pigment material adsorbed.

Our TLC separation of hydrocarbon from non-hydrocarbon compounds has been described previously (Quinn and Wade, 1974). Briefly, preparative TLC on Silica Gel G was used for sediment and Arctica samples. The plates were developed in a system of petroleum ether:NH_4OH (100:1) and visualized by bromothymol blue indicator or UV light. The total hydrocarbons were isolated by scraping the region defined by separately co-chromatographed phenanthrene (Rf ≈ 0.5) and n-C_{26} (Rf ≈ 1.0). This method of separation also allows for the isolation of any class of hydrocarbons within the total hydrocarbon region by visually isolating that region of the plate corresponding to a given spotting standard. A common problem encountered in column chromatographic separation is the collection of methyl esters along with the aromatic hydrocarbon fraction. In theory, if a sufficient amount of water is present in the extraction mixtures, saponification should proceed with no methyl esters produced via transesterification. However, if methyl esters are present they are easily separated from the hydrocarbons by TLC, and an occasional poor separation due to deactivation of the silica gel is quickly noted.

The isolated hydrocarbons, obtained by extraction of the silica gel, were analyzed on a Hewlett Packard model 5711 gas chromatograph (GC) equipped with dual flame ionization detectors. Two meter stainless steel (2.2 mm i.d.) packed columns of 12 or 15% FFAP on chromosorb W(HP) were used and hydrocarbon concentrations determined by comparing the area above baseline with that of the internal standard. Two non-polar columns, 2 m stainless steel (2.2 mm i.d.) 4% Apiezon L on chromosorb W(HP) and 2 m stainless steel (2.2 mm i.d.) 2% OV-1 on Anakrom Q, were also used in this study. Hydrocarbons eluting between n-C_{14} and n-C_{34} were routinely quantified. Further details of the GC methodology are found in Quinn and Wade (1974).

Organic Carbon Analyses

Approximately 10 g of wet sieved sediment were treated overnight with 3 N HCl to dissolve any carbonate material. The acid was removed by filtration and the sediment was rinsed with distilled water and dried for 4 hours at 100°C. The dried sediment was ground to a fine powder and duplicate analyses performed on a Carlo Erba Model 1100 elemental analyzer.

Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS analyses of selected hydrocarbon extracts were performed on a Finnigan 1015 quadrupole mass spectrometer coupled to a Varian 1400 gas chromatograph equipped with a 10 meter SE-30 glass capillary column.

Infrared and Nuclear Magnetic Resonance Spectroscopy

Infrared (IR) spectra of selected hydrocarbon samples were obtained on a Perkin Elmer model 521 spectrophotometer. NMR (proton) spectra were obtained using varian CFD-20 with a micro proton probe.

PCB Analysis (Polychlorinated biphenyls)

Alumina and silicic acid column chromatography was used to isolate PCB material from the total non-saponifiable extract. Electron capture GC (Tracor Microtek 220, ^{63}Ni detectors) on OV-17/QF-1 and SE 30/QF-1 columns, was used to analyze the PCB fraction. The chromatograms were quantified relative to an Aroclor 1254 standard.

Blanks

Throughout this study reagent and procedural blanks were determined and the reported values have been corrected for these blanks. Arctica sample concentrations were routinely 10 to 30 times the blank value and sediment concentrations ranged from 2 to 430 times the blank value averaging 83 times higher. Samples analyzed without the internal standard showed that natural levels of n-C_{20} were not detectable.

SECTION III

RESULTS

SURFACE SEDIMENTS

The quantities of hydrocarbons present in the surface sediments of R. I. Sound are presented in Table 1. The values range from a low of 1.0 μg/g found in the coarse sands of station 21 having an organic carbon content of 0.72 mg/g, to a high of 301 μg/g found on the southern flank of the dredge spoil site (Station 4) with an organic carbon concentration of 8.65 mg/g.

The precision of the values given in Table 1 should be considered as follows. The precision of the analytical method and chromatographic analysis is ±5%. Analyzing duplicate samples from the same subsample (i.e. same wet sieved subsample) yields an average precision of ±9.4%. Comparing the results from two separate subsamples of the same grab sample indicates that the subsampling precision is ±18.5% on the average. Replicate grab samples taken at the same station vary by ±26.3%. Farrington (1971) reported an average variability of ±29% for hydrocarbon analyses of replicate sediment dredge haul samples from Narragansett Bay.

Figure 2 illustrates representative gas chromatograms of hydrocarbons from R. I. Sound Arctica islandica, R. I. Sound surface sediment and Providence River surface sediments adjacent to the Field's Point sewage outfall (2a, b, c respectively). R. I. Sound surface sediments consist of from 72.5 to 97% of an unresolved complex mixture (UCM) of hydrocarbons (Table 1). This UCM consists of chromatographically coeluted naphthenic, naphthenoaromatic, and aromatic hydrocarbons and is characteristic of an anthropogenic assemblage of hydrocarbons (Farrington and Meyers, 1975; Farrington et al., 1977a). Superimposed above the UCM are two prominent peaks (X and Y, Fig. 2b). These compounds contain only carbon and hydrogen as revealed by infrared spectroscopy. In addition, combined gas chromatography/mass spectrometry (GC/MS) reveals that they are cycloalkenes of molecular weight 348 (C_{25} H_{48}) and 344 (C_{25} H_{44}) in the order of elution. These compounds are identical to those reported by Farrington et al. (1977a) in Buzzards Bay and Gulf of Maine sediments and appear to be very similar, if not identical to those reported by Gearing et al. (1976) in Gulf Coast sediments. The cycloalkenes are also observed in the surface sediments of Narragansett Bay as confirmed by GC/MS (this study). The sedimentary compound reported by Farrington and Quinn (1973a) having a retention index on Apiezon L of 2023 appears to be the 344 compound. The mass spectra of the 344 compound (HC 344) is given in Figure 3 and further

Table 1. Hydrocarbon content of Rhode Island Sound surface sediments.

Station no.	Total hydrocarbons (µg/g dry weight)	Organic Carbon (mg/g dry wt.)	% UCM	HC_{344} (µg/g dry)
1 (0-4 cm)	18.4	--	--	
1 (4-8 cm)	184	11.0	86.1	0.13
2	116	5.62	95.0	0.27
3	53.5	4.51	92.6	0.58
4	301	8.65	97.0	1.01
8	21.0	1.55	86.5	0.65
9	104	5.24	94.0	1.51
15	46.1	3.13	92.0	1.19
16	96.2	3.76	95.0	1.04
17	43.9	4.90	89.0	1.38
18	22.9	3.75	90.0	1.01
19	21.1	3.60	89.5	1.01
20	4.0	0.20	86.0	0.10
21	1.0	0.72	72.5	0.03
30	29.7	3.54	93.4	1.03
31	7.6	0.88	91.2	0.19
40	56.1	5.36	90.5	1.51
43	27.1	4.65	85.5	1.08
44	20.8	2.12	91.0	0.88
45	46.8	3.73	91.1	0.94
46	13.9	2.38	91.0	0.69
50	51.2	5.79	92.5	1.55

UCM = unresolved complex mixture of hydrocarbons.

Figure 2. Representative gas chromatograms of R. I. Sound *Arctica islandica* specimens (a); R. I. Sound surface sediment (b); Providence River surface sediment adjacent to sewage outfall (c) (G. C. data: 2 meter stainless steel column containing 12% FFAP on Chromosorb W(HP), temperature programmed from 100-250°C at 8°C per minute)

Note: 20 = internal standard ($n\text{-}C_{20}$)

25-31 = n-alkanes of that carbon number

X = cycloalkene, (MW = 348)

Y = cycloalkene (MW = 344)

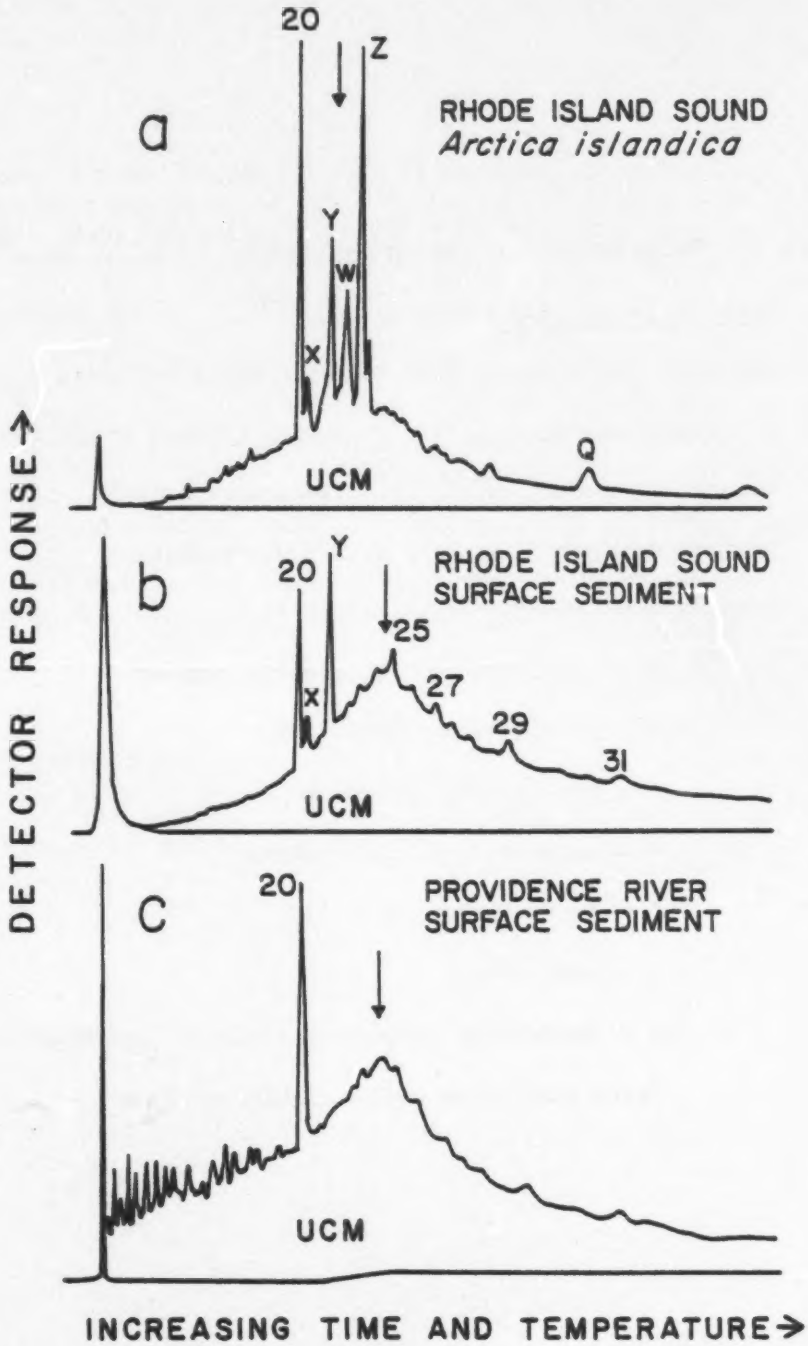
W = unidentified cycloalkene

Z = cycloalkene (MW = 342)

Q = squalene

UCM = unresolved complex mixture of hydrocarbons

Arrow indicates point of UCM maximum.


20
Z
a
RHODE ISLAND SOUND
Arctica islandica
Y
W
X
Q
UCM
DETECTOR RESPONSE→
b
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RHODE ISLAND SOUND
SURFACE SEDIMENT
25
X
27
29
31
UCM
c
20
PROVIDENCE RIVER
SURFACE SEDIMENT
UCM
INCREASING TIME AND TEMPERATURE→

information on HC 344 and HC 348 is tabulated in Table 2. Farrington et al. (1977a) have reported similar spectra. The mass spectra reveal alkene, cycloalkane and terpene features with the 348 compound containing one ring and the 344 possibly two rings.

The most prominent compound, HC 344, appears to consist of a bicyclic core with two branched aliphatic side chains. The geochemical stability of HC 344 implies that at least one of the two double bonds is exocyclic and is stabilized by the ring structure. Its infrared spectrum reveals two olefinic structures; trisubstituted (815 cm^{-1}) and vinyl (885, 910 cm^{-1}). The lack of a ~970 cm^{-1} absorption indicates the absence of any trans-disubstitution. Proton NMR spectrometry indicates a $>C = CH_2$ structure. One of the two protons in this vinyl group appears to be deshielded (δ = 6.8 ppm) by an adjacent olefin (perhaps cyclic). This downfield shift (6.8 ppm) is indicative of a conjugated structure. The chemical shift of the other proton is 4.7 ppm (δ).

Quantities of HC 344 vary from station to station (Table 1) but are highly correlated with the organic carbon content of the sediment ($r = 0.955$) as shown in Fig. 4. Note that the four stations not showing this strong correlation, numbers 1, 2, 3, 4, are found within the disposal site (Fig. 1).

HC 344 and HC 348 are found throughout Narragansett Bay and Rhode Island Sound sediments. Analyses of phytoplankton, zooplankton, particulate matter and dissolved hydrocarbons, do not reveal either of these compounds, although the ocean quahog Arctica islandica (to be discussed below) and Mercenaria mercenaria the large bivalves of the Sound and Bay respectively contain these and other similar structures.

Figure 2b shows that the resolved n-alkanes n-C_{25}, C_{27}, C_{29} and C_{31} are also present in the sediments. However,the resolved components, mainly consisting of these alkanes which have their origins in terrestrial plants, (Farrington and Meyers, 1975), and the two cycloalkenes, constitute at most 15% and more typically 10% of the surface sediment total hydrocarbons.

Throughout Narragansett Bay the UCM is a major feature of recent sedimentary hydrocarbons (Farrington and Quinn, 1973a) as well as of suspended hydrocarbons in the water column (Schultz, 1974). A comparison of the chromatograms of R. I. Sound sedimentary hydrocarbons Fig. 2b with those from the Providence River, Figure 2c, reveals that the latter shows considerably greater quantities of low boiling resolved and unresolved features, typical of those from the Fields Point sewage treatment plant effluent (Farrington, 1971; Farrington and Quinn, 1973b; Van Vleet and Quinn, 1977). However, analyses of surface sediments from areas of Narragansett Bay proper (Farrington and Quinn, 1973a; Wade unpublished data; Van Vleet and Quinn, 1977) indicate that these lower boiling components are rapidly lost through weathering and an assemblage similar in boiling point distribution to R. I. Sound sediments (Fig. 2b) is found in the Bay, and elsewhere in the Providence River.

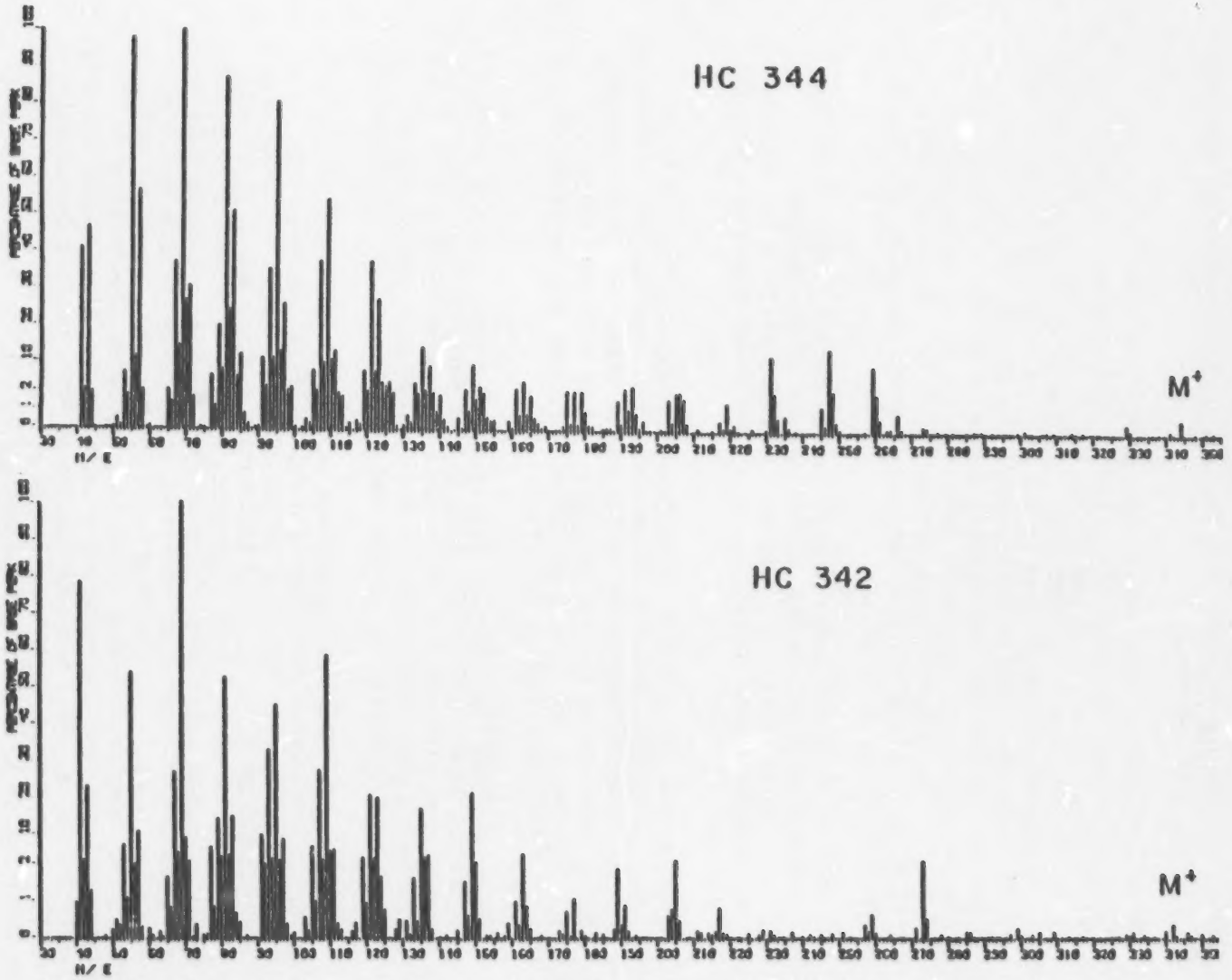

Figure 3. Mass spectra of unknown compounds; Compound Y; HC 344; sediments and Arctica Compound Z/ HC 342; Arctica.

Table 2. Relevant data on cycloalkene compounds.

Compound[1]	Location	Molecular Weight	Mass Spectral Data: Low Mass Fragments	Mass Spectral Data: High Mass Fragments	Retention Indices (Kovats, ±5): 12% FFAP	Retention Indices (Kovats, ±5): 4% Apeixon L	Retention Indices (Kovats, ±5): 2% OV-1
X	Sediments, Arctica	348	41,55,57,67,69,81, 83,85,95,97,109, 111,123	207,235, 250,266	2030	--	2025
X (hydrogenated)		350	43,55,57,69,71,83, 85,97,99,111,113,125	210,238, 266,280	2020	--	2125
Y	Sediments, Arctica	344	41,43,55,57,69,81, 83,93,95,97,107, 109,121,123	231,247, 259,273, 329	2170	2020	2080
Y (hydrogenated)		348	NA	NA	2065	2070	2145
Z	Arctica	342	41,43,55,57,67,69, 79,81,83,93,95,107, 109,121,123	205,217, 259,273	2330	--	2170
Z (hydrogenated)		350	NA	NA	2010	--	2110

[1]Compound designation refers to Figure 2.

NA = not analyzed

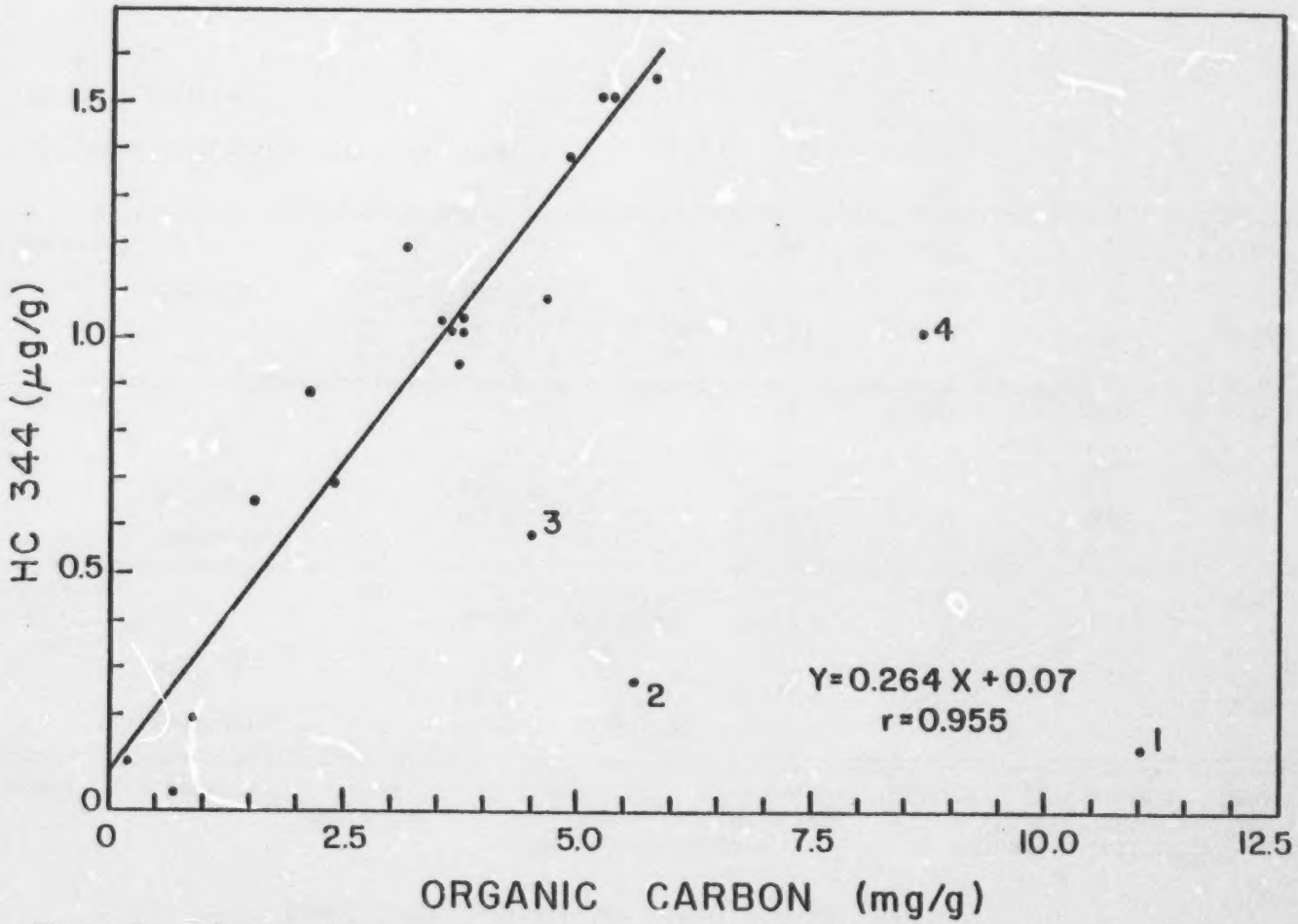

Figure 4. Relation of organic carbon content of sediment to concentration of compound Y (HC 344) in sediment.

The relation between surface sediment total hydrocarbon and organic carbon contents is illustrated in Fig. 5. Excluding stations 1, 2, 4, 9 from the spoil site and station 16 adjacent to the site, hydrocarbon concentrations correlate positively ($r = 0.855$) with organic carbon content. Including these five stations decreases the correlation coefficient to $r = 0.72$ but more importantly results in an unrealistic regression intercept of minus 41 μg hydrocarbon/g. Farrington's (1971) stations located at the entrance to Narragansett Bay and on the Continental Shelf south of R. I. Sound (40°50'N, 71°00'W) fall very close to the regression line shown in Fig. 5. The ratio of hydrocarbon to organic carbon may be a useful parameter in comparing both the nature and health of the sedimentary environment in different areas as shown in Table 3. Ratios vary from highs of 5.55 in the Providence River and 10.7 within the dredge spoil deposit (having its source in the Providence River), to 2.03 in lower Narragansett Bay, decreasing to 0.96 in Rhode Island Sound. The surface sediments in the disposal area compare well with lower Narragansett Bay values for this parameter. For comparison, other nearshore and continental shelf values from the region are given in Table 3. Buzzards Bay appears to be related to adjacent Rhode Island Sound when considering this parameter (0.63 vs. 0.96).

The hydrocarbon and organic carbon values at our Station 40 and at Station WR of Farrington and Quinn (1973a) are in excellent agreement (hydrocarbons = 56.1 and 60 μg respectively; organic carbon = 5.36 and 5.63 mg/g respectively). The two stations are in very close proximity to one another and in spite of different extraction procedures utilized on samples taken 5 years apart, similar results are obtained.

SEDIMENT CORES

Figures 6 and 7 illustrate the differences between the core from Station 17 and that from the flanks of the dredge spoil deposit (Station 4). Below 18 cm in the Station 17 core (Fig. 6) the resolved components, notably the n-alkanes n-C_{25}, C_{27}, C_{29} and C_{31} emerge from the unresolved background and the percentage of the UCM, as well as the total hydrocarbon concentration, decreases with depth (Table 4). As the total hydrocarbon content and the percentage of UCM decrease with depth in the core, the sum of the odd n-alkanes, n-C_{25} to n-C_{31}, does not decrease markedly (Table 4; Figure 6). The quantity of HC 344 does decrease with depth, while the organic carbon concentration, after sharply falling off below the top 8 cm, remains constant with depth.

Unlike the Station 17 core, the core from Station 4 (Fig. 7) shows a rapid increase of both total hydrocarbon concentration and organic carbon content with depth (Table 4). The order of magnitude increase in hydrocarbon concentration within the dredge spoil mound can be ascribed to the fact that the origin of much of the spoil comes from the Providence River sediments which contain 1-6 mg/g of total hydrocarbon (Farrington and Quinn, 1973a; Farrington, 1971; Van Vleet and Quinn, 1977). Furthermore, the sequence of spoil deposition resulted in the more highly contaminated spoil being blanketed by cleaner material from areas of the Providence navigation channel, lower in hydrocarbon concentration (Saila et al., 1972).

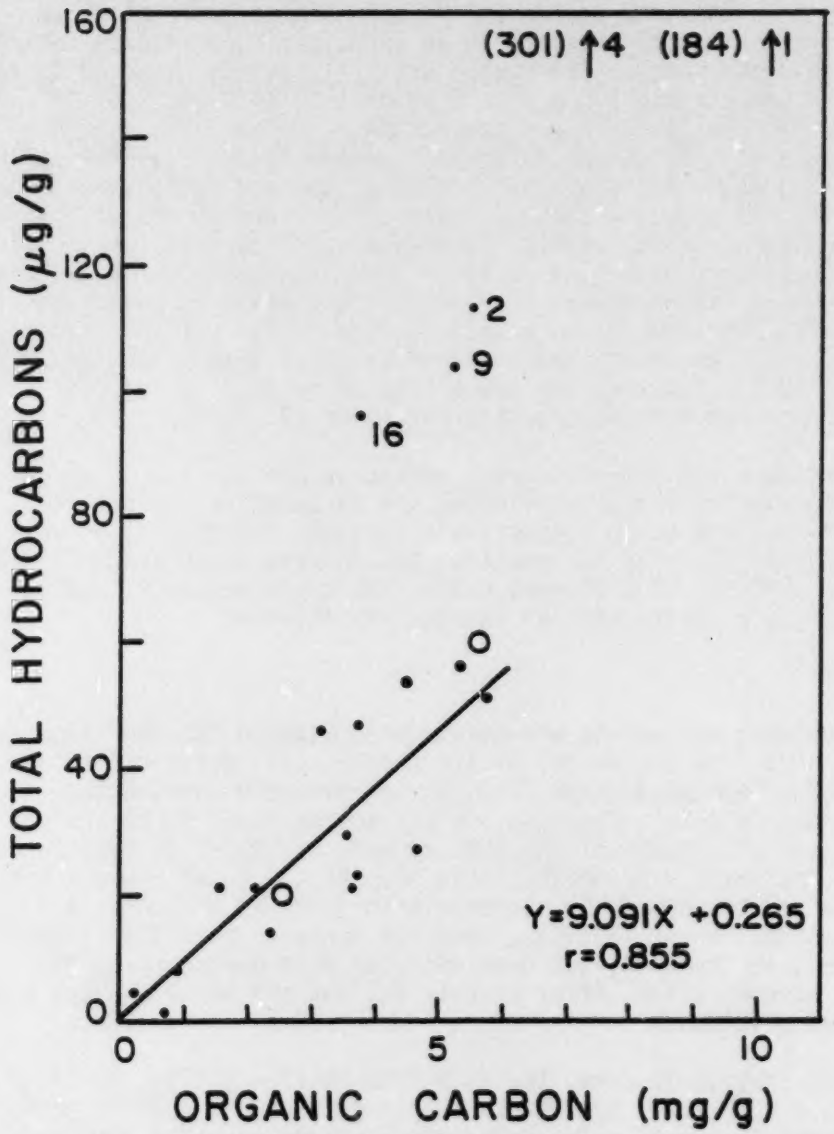

Figure 5. Relation of organic carbon content of sediment to its total hydrocarbon content. Points denoted by open circle from Farrington (1971).

Table 3. Hydrocarbon concentrations relative to organic carbon contents of R. I. Sound and Narragansett Bay sediments.

Location	Hydrocarbon:Organic carbon[1]	
	Average	Range
Providence River[2]	5.55	5.54-5.56
Upper Narragansett Bay[3]	5.19	3.17-7.21
Lower Narragansett Bay[4]	2.03	1.76-2.31
R. I. Sound (this study)[5]	0.96	0.14-2.00
Spoil Site (surface grabs)[6]	2.35	1.67-3.48
Spoil Site (core 0-45 cm)[7]	10.7	5.14-17.9
Buzzards Bay[8]	0.63	---
Gulf of Maine[8]	0.29	---
Hudson Canyon[8]	0.19	---

[1]Concentration of (hydrocarbons [mg/g]/organic carbon [mg/g]) x 10^2 or percentage of organic carbon as hydrocarbon.

[2]Stations FP, E_1 (Farrington and Quinn, 1973a).

[3]Stations E_2, D (Farrington and Quinn, 1973a).

[4]Stations A, B, C (Farrington and Quinn, 1973a).

[5]Excluding stations 1, 2, 4, 9, 16.

[6]This study, stations 1, 2, 4, 9, 16.

[7]Values increase with increasing depth in core.

[8]Farrington et al. (1977a).

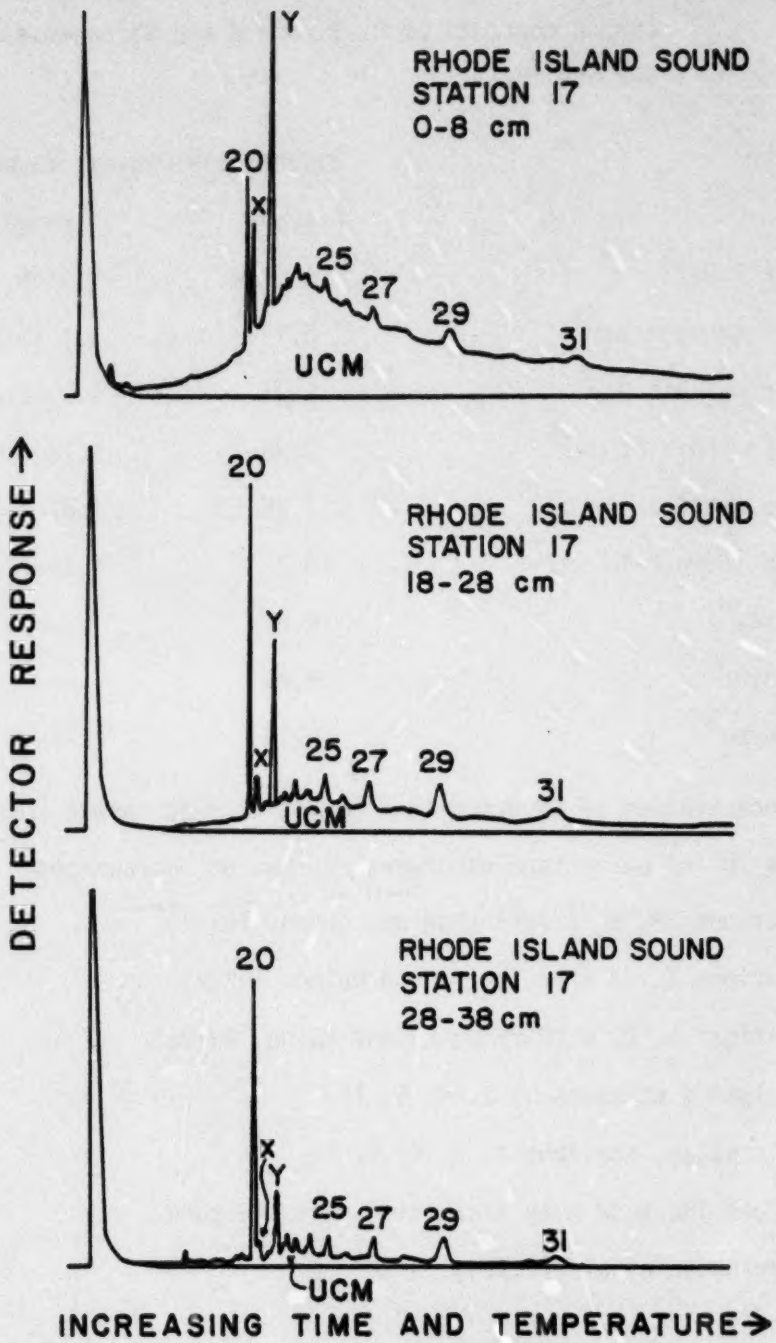

Figure 6. Gas chromatograms of hydrocarbons in sediment core from Station 17. X and Y and 20 defined in Figure 2. G. C. conditions as in Figure 2.

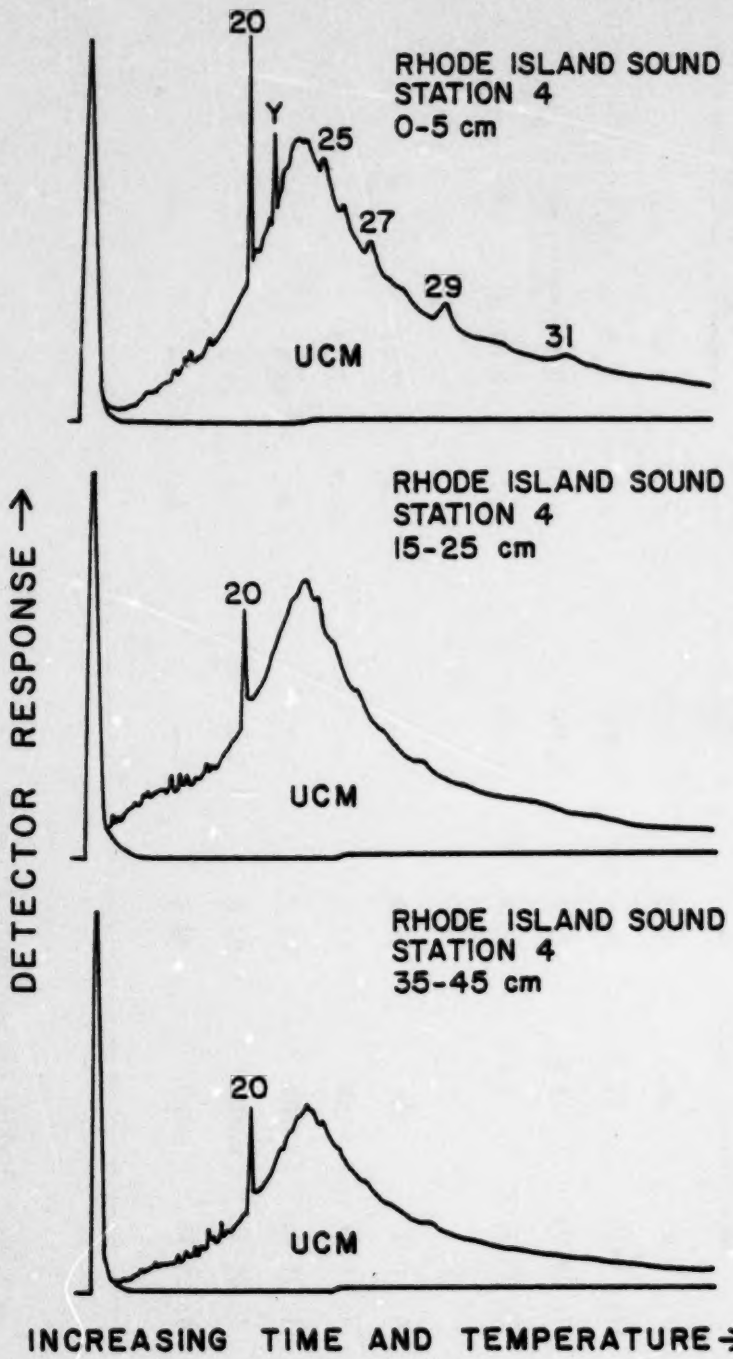

Figure 7. Gas chromatograms of hydrocarbons in sediment core from Station 4. X and Y and 20 defined as in Figure 2. G. C. conditions as in Figure 2.

Table 4 Hydrocarbon Content of Rhode Island Sound Sediment Cores.
(Dry weight basis)

Core No.[1]	Total Hydrocarbons (µg/g)	%UCM[2]	$n\text{-}C_{25,27,29,31}$ (µg/g)	HC 344 (µg/g)	Organic Carbon (mg/g)	PCB (ng/g)
17: 0-8	38.5	93.8	0.483	1.49	3.50	8.5
17: 8-18	21.1	93.4	0.445	0.51	2.49	3.1
17: 18-28	4.6	79.7	0.340	0.24	2.51	nd
17: 28-38	2.4	38.8	0.380	0.13	2.61	nd
4: 0-5	184	96.0	---	0.68	3.57	---
4: 5-15	486	98.0	---	0.44	7.33	---
4: 15-25	1100	98.0	---	nd	13.5	---
4: 25-35	2400	98.0	---	nd	13.6	---
4: 35-45	2270	98.6	---	nd	14.4	---

[1]Core No. = Station Number:Depth Range(cm)

[2]UCM = Unresolved Complex Mixture of hydrocarbons.

nd = None Detected

The location of Station 4 is on the southern flank of the dredge spoil mound (Fig. 1) and consists of the earlier deposited material in contrast to the residual gravelly lag material located atop (0-4 cm) the mound (Station 1) of markedly lower hydrocarbon concentration (18.4 μg/g, Table 1).

The 35-45 cm section of core No. 4 (Table 4) contains 12% aromatic hydrocarbons as separated by thin layer chromatography and analyzed by gas chromatography. This value is slightly lower than that of the Providence River surface sediments (∿18%) probably due to weathering effects. By contrast, the surface sediments of R. I. Sound contain lesser quantities of aromatics (2-9% of the total).

The Station 17 core was analyzed for its PCB content (Table 4). PCB compounds were present through the top two sections and disappear below 18 cm. The surface value (8.5 ppb) is two orders of magnitude lower than Providence River surface sediment values (Paulson, personal communication).

The gas chromatographic pattern of the hydrocarbons in the Station 4 core, Fig. 7, mainly shows a broad UCM assemblage. The prominent resolved feature in the 0-5 cm section, HC 344, is either absent deeper within the core or else is swamped by the UCM input. At the point of origin of the spoil material, the Providence River, HC 344 is not observed in the sediment gas chromatograms (Farrington and Quinn, 1973a; Van Vleet and Quinn, 1977). Although not exhibiting the strikingly low boiling resolved features which are typical of Providence River sediment samples adjacent to the municipal sewage outfall (Van Vleet and Quinn, 1977), (Fig. 2c), core 4 does contain low boiling unresolved features that are not commonly found in samples outside of the spoil disposal site (Fig. 7, 15-25 cm vs Fig. 2b and Fig. 6).

ARCTICA ISLANDICA

A typical gas chromatogram of the hydrocarbons found in the ocean quahog of Rhode Island Sound is shown in Fig. 2a. These hydrocarbons differ from those in the adjacent sediments. First, there are at least five biogenic hydrocarbons present in the clams. Examination of these compounds by combined GC/MS reveals that HC_{348} and HC_{344} also are found in the clams. The mass spectra of these compounds and their hydrogenation products are identical to the cycloalkenes found in the sediments. Furthermore the predominant peak in Fig. 2a, (Z), appears to be another related cycloalkene of molecular weight 342. This compound appears to have four double bonds and one ring as it hydrogenates to a molecular weight of 350. Its mass spectra is given in Fig. 3 (HC 342). Additional relevant data on retention indices are presented in Table 2. Other compounds in the C_{20}-C_{24} range include as many as five other cycloalkenes of undetermined molecular weight and two phytadienes which upon hydrogenation yield a substantial phytane peak.

A more fundamental difference between the Arctica and sediment chromatograms lies in the elution range of the UCM. As the arrows indicate in Fig. 2, the Arctica UCM gives a maximum detector response at approximately a retention time corresponding to n-C_{23}, while the sediment UCM, at the

same temperature and gas flow rate conditions, peaks at n-C_{25}. Similar differences have been noted in Narragansett Bay (Boehm and Quinn, unpublished; Farrington and Quinn, 1973a) where the common bay quahog Mercenaria mercenaria exhibits a lower UCM boiling point distribution than do the sediment hydrocarbons in which the organism lives. Teal and Farrington (1977) also noted that the hydrocarbon boiling point distribution in mussels is lower than that in the adjacent sediment. Other than the coexistence of HC 344 and HC 348 in the clams and sediments, Arctica does not reflect the sedimentary hydrocarbon assemblage.

Arctica specimens from R. I. Sound contain on the average 81% UCM in their hydrocarbon assemblage, and contain 9-17% aromatic hydrocarbon material as separated by TLC procedures outlined in Boehm and Quinn (1974).

Hydrocarbon concentrations in whole Arctica samples range from 2.60 to 6.37 µg/g wet weight (Table 5). Thus, the range of concentrations varies by only a factor of 2.5 throughout the study area whereas analyses of surface sediments show a range of concentrations over two orders of magnitude. The lack of correlation between surface sediment hydrocarbon concentrations and Arctica values is best illustrated by the low station 4 Arctica and high sediment values. The highest clam values are found nearer the mouth of Narragansett Bay (Sta. 44 = 6.37 µg/g) and at Station 8, 0.5 km southeast of the disposal site (6.12 µg/g). For comparison M. Mercenaria specimens contain approximately 14-16 µg/g at a Providence River station (Farrington and Quinn, 1973a) and 4.1-10.0 µg/g at Station C midway down the Bay and 2.9 to 3.5 µg/g at Station A in Fig. 1 (Table 5).

There is no systematic variation in Arctica's hydrocarbon concentration with distance from the dredge spoil site. The nature of the gas chromatograms remains constant throughout the study area. In general higher hydrocarbon concentrations are seen at stations ranging from the mouth of Narragansett Bay, Station 46, (5.52 µg/g wet), midway between the mouth and the disposal site, Station 44 (6.37 µg/g wet) to the disposal site itself, Stations 1, 3, 8 and 9 (4-6 µg/g wet). Concentrations then appear to drop off on the NW to SE transect (Station 8; 6.12 µg/g wet to Station 22; 2.88 µg/g wet). Concentrations drop off less markedly in the southwest direction from the spoil site, although due to low faunal abundances at Stations 30 and 31 sampling gaps appear.

An interlaboratory intercalibration was undertaken between this laboratory and that of Dr. J. Farrington at the Woods Hole Oceanographic Institute. Approximately 700 g of Arctica homogenate (blended tissues and fluids of ten animals) from Sta. 16 were prepared and subsamples analyzed by both laboratories. Both laboratories employed a saponification-extraction of a homogenized sample under reflux. Quantification by gas chromatography was accomplished using the internal standard method. The main differences in the two methodologies is that a column chromatographic separation of hydrocarbons from other lipid material is employed by the WHOI group (Farrington and Medeiros, 1975). Two fractions, f_1 representing the pentane eluted hydrocarbons, and f_2, that fraction of hydrocarbons eluted by pentane: benzene (4:1) are isolated. Our separation is by TLC in a developing system

Table 5. Hydrocarbon concentrations in *Arctica islandica* of Rhode Island Sound.

Station	Total hydrocarbons[1] (µg/g wet weight)
1	5.75
3	5.46
4	2.95
8	6.12
9	4.04
15	2.84
16	5.32
17	5.53
18	4.57
19	3.06
20	3.62
21	2.62
22	2.88
25	2.60
33	4.05
44	6.37
46	5.52
C	6.54[2]
	4.1-10.1[2,3]
A	3.50[4]
	2.90[3,4]

[1]Precision for above values averages ±20%.

[2]Represents concentrations in *Mercenaria mercenaria* specimens from Narragansett Bay. For station location see Farrington and Quinn (1973a).

[3]Values from Farrington and Quinn (1973a).

[4]Represents concentrations in *M. mercenaria* specimens from Narragansett Bay. For station location see Fig. 1.

of petroleum ether and only the total hydrocarbon fraction is generally isolated and analyzed. Both GC analyses were carried out on packed columns. As shown in Table 6, the qualitative nature of the chromatograms is quite similar showing the same percentages of resolved and unresolved components. Total hydrocarbon values are within 40% of each other which we considered to be in reasonable agreement. This is the first such published intercalibration that we are aware of using whole organisms.

OTHER HYDROCARBON ANALYSES

Qualitative hydrocarbon determinations were performed on several size fractions of plankton from lower Narragansett Bay, on two amphipod species Unciolo irrorata and Leptocheirus pinguis habitating R. I. Sound sediments, on worms (Nereis sp.) in R. I. Sound sediments and on suspended particulate matter in lower Narragansett Bay. We were looking for traces of the cycloalkenes from these sources and found none. The particulate hydrocarbons and the phytoplankton (25 μ net) contain 21:6 (heneicosahexaene) as a prominent component (Lee et al., 1970; Schultz, 1974). Its identity was confirmed in this study by combined GC/MS. One species of amphipod (L. pinguis) contains a prominant polyunsaturated component having the same retention index as 21:6 (2375 on FFAP). Other polyunsaturated hydrocarbons are found in the amphipods and pristane and squalene are major components of the Nereis worms.

Table 6. *Arctica* Hydrocarbon Intercalibration Study.

	U.R.I.	W.H.O.I.
G. C. Column	12% FFAP 2 m stainless steel	OV-17 2 m glass
Total Resolved Components (µg/g wet weight)	1.06	1.54*
Total Unresolved Components (µg/g wet weight)	4.26	5.90*
Total Hydrocarbons (µg/g wet weight)	5.32 ± 0.33 (3 analyses)	7.44 ± 0.09 (2 analyses)
Percent Resolved	20	21
Percent Unresolved	80	79

*sum of contributions of fraction 1 (f_1) and fraction 2 (f_2).

SECTION IV

DISCUSSION

HYDROCARBON BIOGEOCHEMISTRY

In considering the hydrocarbon geochemistry of Rhode Island Sound one is faced with a dilemma. The effect of the dredge spoil disposal sequence, from 1967 to 1970, introducing sediment of high hydrocarbon and organic matter content, must be examined. However, no R. I. Sound sediment samples taken prior to the initiation of disposal are available for hydrocarbon analyses. Thus one must reconstruct the hydrocarbon geochemistry from measurable, diagnostic parameters which one can use to differentiate a "normal" from an "abnormal" Narragansett Bay/R. I. Sound system. To this end we will consider the quantitative and qualitative hydrocarbon chemistry, trends for a single compound, HC 344, and the organic carbon content of the sediments.

The unresolved low boiling hydrocarbons found in the Providence municipal sewage effluent (Farrington, 1971), in Providence River sediments adjacent to the outfall (Fig. 2c), and within the dredge spoil deposit (Fig. 7) are not seen in surface sediments outside the disposal area (Fig. 2b). These components are soon weathered if exposed to the sediment water interface or resuspended in the water column as evidenced by their disappearance with increasing distance from the Fields Point sewage outfall (Van Vleet and Quinn, 1977). However, if large scale movement of dredge spoil material had taken place in R. I. Sound we would see evidence of these components at stations near the disposal site (e.g. station 17). This is not the case (Fig. 2b and 6).

The absolute quantities of hydrocarbons in the R. I. Sound surface sediments (Table 1) can not be used directly to evaluate dredge spoil hydrocarbon movement because of the variations in sediment type and sedimentation rates throughout the study area (McMaster, 1960; Collins, personal communication).

Considering the hydrocarbon:organic carbon relation (HC/OC) (Table 3), while the hydrocarbons comprise 5.5% of the organic carbon in the polluted Providence River sediments, this value falls off rapidly through the estuary decreasing from 5.5% to about 2% at Station A at the mouth of the Bay. At Station 40 and Station 46 in R. I. Sound the value decreases to 1.5 and 0.6% respectively. It appears that most of the hydrocarbons are associated with particles that settle in the Bay. The silty material, only some of which settles at the mouth of the West Passage of Narragansett

Bay (Collins, 1976) is depleted in hydrocarbons relative to total organic carbon, due to inputs of organic carbon from natural sources which contain a smaller amount of hydrocarbons relative to Providence River inputs. The fine particulate material reaching R. I. Sound waters has also been subjected to greater microbial alteration of its HC/OC ratio probably due to both its longer residence time in the water column and its greater surface area per unit weight. The distribution of particulate hydrocarbons in Narragansett Bay, which shows a decreasing concentration with increasing distance from the Providence River, correlates well with that predicted from a circulation model of the Bay (Schultz, 1974) using the upper Providence River area as the only source of hydrocarbons to the estuary. However, dilution by natural sources of organic carbon within the Bay would alter the HC/OC ratios of the particulate matter. Zafiriou (1973) determined the ^{14}C content of the hydrocarbons from Station E-1 of the Providence River, and reported an average age of 24,400 years indicating that the hydrocarbon chemistry at this station was defined by 80-97% anthropogenic material and 3-20% recently biosynthesized compounds.

The covariance of surface sediment hydrocarbon and organic carbon concentrations (Fig. 5) and the relative uniformity of the HC/OC ratio throughout the R. I. Sound study area are in sharp contrast to the anomalous behavior of stations 1, 2, 4, 9 and 16 which are located at or adjacent to the disposal site. The quantity of organic carbon in the sediment is a function of the sedimentation rate as well as other factors. Since total hydrocarbon concentrations covary with organic carbon it appears that hydrocarbons reach the sediments via normal sedimentation in the Sound. The sedimentation rate throughout the study area probably varies considerably due to physical factors, and controls the absolute hydrocarbon concentrations. However, a consideration of the HC/OC ratio normalizes this variable and permits a comparison of different stations. Based on this argument, the only sampling stations to be affected by an input of dredge spoil material, which has ten times the HC/OC ratio (Table 3), are stations 1, 2, 4, 9 at the disposal site and station 16, one kilometer to the southwest.

Figure 4 illustrates that the biogenic compound, HC 344, covaries very significantly with organic carbon at all stations except 1, 2, 3, and 4. This compound (to be discussed below) serves as an excellent marker of normal biogenic and/or diagenetic activity in the sediments of this region. When used in conjunction with organic carbon to normalize the heterogeneity of the sediments, (Fig. 4), it is apparent that the effect of the high hydrocarbon dredge spoil material on the benthic environment of R. I. Sound is confined to an area within 1-2 km of the disposal site.

The apparent lack of contribution of dredge spoil material to R. I. Sound's hydrocarbon geochemistry, as evidenced in the preceding paragraphs is a surprising result. Enough spoil was deposited to theoretically cover the entire study area ($\sim$150 km^2) with a 4.2 cm layer of sediment with a high hydrocarbon content. However, it appears that much of the material settled rapidly and cohesively upon dumping and that little has been re-suspended since. Alternatively it can be postulated that resuspension of dredge spoil has taken place, but that this material is carried out of the

study area by bottom currents. Gordon (1974) found that 99% of a dredge spoil deposited in Long Island Sound settled cohesively and initially remained within a 120 meter radius of the impact point. Visual observations of the R. I. Sound dredge spoil disposal site (Saila et al., 1972) indicated that an erosion resistant deposit resulted and large scale resuspension had not occurred. This observation is verified chemically by this study. The presence of lag deposits on the top of the deposit indicates that some erosion has most likely occurred. However, if erosion has proceeded, there is no evidence that the eroded material settled within the study area.

Analyses of Arctica islandica indicate that their hydrocarbon contents are probably due to a combination of ingestion of particles from the water column and biosynthesis. The most important influence on their hydrocarbon content appears to be distance from Narragansett Bay and hydrocarbon sources therein. Quantitative and qualitative distributions of hydrocarbons in these clams suggests a small (if any) input of dredge spoil hydrocarbons. It is possible that the initial disposal sequence introduced hydrocarbons to the clams, but in the five year interim before sampling for this study commenced, the Bay's influence has been reasserted. Certainly, the hydrocarbon content of Arctica islandica throughout the study area is comparable to that in Mercenaria mercenaria commonly harvested in lower Narragansett Bay (Table 5). All animals contain some indication of an anthropogenic assemblage of hydrocarbons, having their probable source in chronic inputs from the Providence River and urban atmospheric fallout within the Narragansett Bay drainage basin.

The lower boiling point distribution of hydrocarbons exhibited in the clams relative to the sediments, Fig. 2a and 2b, may be explained by 1) differing sources; 2) biochemical degradation or modification; 3) selective uptake by the clams; 4) selective solubilization of certain hydrocarbons out of the sediments followed by uptake by the clams, and 5) a variation of the qualitative hydrocarbon assemblage with sediment grain size and selective ingestion of certain resuspended particle sizes by the clams. While none of these explanations can be completely ruled out, the gas chromatographic similarity of particulate hydrocarbons in the water column (Schultz, 1974) with those in the sediments casts doubt on the first explanation. However, Thompson and Eglinton (1976) found that some estuarine benthic diatoms exhibited a lower boiling range of aliphatic hydrocarbons than was seen in the sediments. Their ingestion by the clams could result in a lower boiling mixture of unresolved hydrocarbons in the clams' fluids and tissues.

Biochemical degradation of anthropogenic hydrocarbons is not known for bivalves although the possibility of their metabolic alteration of hydrocarbon patterns has been discussed (Lee et al., 1972; Stegeman and Teal, 1973). Solubilization phenomena in sea water (Boehm and Quinn, 1973) can result in selective mobilization (Boehm and Quinn, 1974) and selective uptake (Boehm and Quinn, 1976) of classes of hydrocarbons by marine filter feeders, but details of the partitioning of hydrocarbon species between a soluble state, a solubilized (colloidal) state and the adsorbed state are not known. Lee (personal communication) found most hydrocarbon material in

a controlled ecosystem experiment (CEPEX) using No. 2 fuel oil to be adsorbed to particles. However, a possibility that should be studied, is that given the relatively high dissolved organic carbon (DOC) of interstitial waters, sediment resuspension or normal leaching by bottom currents could effect a solubilization of adsorbed hydrocarbons by this level of DOC (Boehm and Quinn, 1973). Furthermore, low level dissolution (thermodynamic solubility) of certain hydrocarbons corresponding to a clam-like assemblage may occur and these hydrocarbons taken up via equilibration across outer membranes of the clam.

A qualitative as well as quantitative fractionation of lipid materials adsorbed to sediment particles can occur in sediments. Finer particles generally are richer in adsorbed organic matter, which includes hydrocarbons, on a comparable weight basis because of a larger surface area. In addition, hydrocarbon distributions can vary qualitatively with grain size within a given sediment (Thompson and Eglinton, 1977) and the adsorption of hydrocarbons can be a function of mineral type (Meyers and Quinn, 1973). However, the sediments in much of the study area are comprised of well sorted sands and the contribution of silt and clay to total sediment is small (McMaster, 1960). Sediment size variation and selective uptake by the clams probably can not alone account for the observed hydrocarbon pattern variations between the clams and the sediments. Also, given the strong affinity of hydrocarbons for solid surfaces, ingestion of whole sediment particles may not result in any transfer of hydrocarbons from the sediment particle to the clam tissues. These particles, with their adsorbed hydrocarbons, may be rejected by the clam without hydrocarbon transfer.

Farrington and Quinn (1973a) suggested that the patterns observed in bivalves may reflect a preserved state of the original suspended matter while diagenetic changes in the sediments could result in the observed higher boiling hydrocarbon assemblage. However, except for certain biogenic compounds there is no evidence that the chromatographic character of the particulate hydrocarbons differs from the distribution in the sediments (Schultz, 1974; this study). Farrington and Quinn (1973a) also mentioned that a selective uptake process by the clams could account for the observed hydrocarbon patterns. Teal and Farrington (1977) noted that filter feeding pelecypods from chronically polluted waters exhibit hydrocarbon distributions appreciably lower in GC retention time than those in the surface sediments. However, Uca pugnax, the fiddler crab, a deposit feeder, seemed to directly reflect hydrocarbon distributions in the sediments.

CYCLOALKENE COMPONENTS

Two of the three main compounds identified in this study, HC 348 and HC 344 (X and Y of Fig. 2) are identical to those examined by Farrington and Tripp (1975), and Farrington et al. (1977a) in other estuarine and continental shelf sediments. The major component HC 344 ($C_{25}H_{44}$), probably having a bicyclic core with two aliphatic side chains, is not found in the water column. It is probably produced in the sediments via biochemical synthesis or through diagenetic alteration of a sedimented biogenic compound or suite of compounds. Despite its olefinic structure, it is relatively

stable, being found at least to a depth of 40 cm within the sediment (see Fig. 6). Its concentration strongly covaries with organic carbon (Fig. 4). Diagenetic alteration of biosynthesized material (e.g. β-carotene, $C_{40}H_{56}$ or squalene, $C_{30}H_{50}$) via chain cleavage and cyclization could possibly result in a series of C_{25} cycloalkene components due to abiogenic processes. De novo synthesis of these compounds by marine microorganisms or their formation via secondary metabolism might also account for the covariance of organic carbon and the cycloalkenes. However, biosynthetic pathways leading to formation of these compounds are not clear, and chemical precursors which yield these cycloalkenes as secondary metabolites are unknown. Whatever their source, these compounds are key components in the sediments and theoretically could be used as indicators of sedimentary processes once more information on their structure and kinetics of their degradation are known.

Other cycloalkenes are found in the bivalve Arctica islandica (Fig. 2a) and the major biogenic component HC 342 ($C_{25}H_{42}$) is not present in the sediment and is indeed quite labile as indicated by its rapid disappearance from unrefrigerated samples. It is obviously protected from degradation within the organism. Whether HC 342 is synthesized by Arctica or by microorganisms in its gut, or whether its taken up as an early labile precursor of HC 344 and HC 348 and thereby preserved is not known.

An explanation of the sediment/Arctica cycloalkene relationship that can not be excluded is that this bivalve, and perhaps other species in this region, are controlling the cycloalkene content of the sediment. HC 344, 348 and 342 (among other cycloalkenes) may be produced in the clams via biosynthetic pathways. The fecal material from these bivalves may contribute significantly to the low organic carbon content of the surface sediments, and may introduce cycloalkenes of biosynthetic origin. The more labile structures are soon degraded in the sediments leaving HC 344 and HC 348.

SEDIMENT CORES

The hydrocarbon profiles in Core 17 (Fig. 6) are strikingly similar to those of Farrington et al. (1977a) and Wakeham and Carpenter (1976). The decreasing concentration of unresolved components with increasing depth is not due to postdepositional alteration. The relative constancy of the C_{25} through C_{31} n-alkanes with depth (Table 4) illustrates that degradation and mobilization of hydrocarbons within the sediments has not been very significant, a conclusion in agreement with that of Farrington et al. (1977a). These components (n-alkanes) would be more readily degraded (Ahearn and Meyers, 1973) and/or solubilized by interstitial organic matter (Boehm and Quinn, 1973) than would components comprising most of the UCM. However, the UCM decreases markedly with depth, not the n-alkanes.

A rapid appearance of an anthropogenic assemblage comprising the UCM in our undated core 17 (Fig. 6) and in the dated cores of Farrington et al. (1977a) in Buzzards Bay and Wakeham and Carpenter (1976), in Lake Washington, probably coincides with the increased usage of petroleum which occurred at the onset of the industrial revolution in North America at the

end of the nineteenth century. This marker is seen within the 18-28 cm section of our Station 17 core. Likewise, PCBs first appear in the 8-18 cm section of the same core. Manufacturing of PCBs began 45 years ago (Hubbard, 1964). Their presence in this 8-18 cm section may reflect both normal deposition plus mixing from the surface section by bioturbation, but absence of PCBs below this section rules out large scale mixing. Based on the infaunal assemblage in R. I. Sound (Saila et al., 1972; Pratt, personal communication) bioturbation is unlikely to proceed to a depth greater than 10 cm. Therefore the hydrocarbon profiles of Fig. 6 and Table 4 are not a result of large scale mixing throughout the 38 cm section.

The exact depth in the core at which the hydrocarbon and PCB markers occur is not known due to the rather broad sampling interval that we chose within the core. Furthermore, bioturbation would tend to blur these chemical markers. The depth of both markers (d) is a function of the sedimentation rate(s) and the depth to which mixing occurs (m):

$$d = ts + m,$$

where t is the historical time elapsed since the introduction of the markers. Two simultaneous equations, one for hydrocarbons and one for PCBs can be solved, giving a sedimentation rate(s) and a bioturbation depth (m). By utilizing two suitable markers we essentially eliminate the bioturbation blurring effect as both markers would have been influenced equally when within the mixing zone. Then we can compute a sedimentation rate which actually accounts for deposition between the two markers. Allowing for the sampling interval uncertainty (18-28 cm for the hydrocarbons and 8-18 cm for the PCBs) and for variations in t, (75-100 years for hydrocarbon introduction, and 30-45 years for PCBs), sixteen solutions are obtained for s and m which indicate the possible ranges for these parameters. Rejecting negative m solutions and sedimentation rates of zero, the possible deposition rate (s) ranges from 1.4-3.3 mm/year and the biological mixing depth from 1.4-13.8 cm at this station in R. I. Sound.

A complete analysis of the recent pollen content of this same core (C. Bernabo, personal communication) indicated that the entire core contained greater than 10% herb pollen, indicative of a post agricultural revolution assemblage. Thus the entire core is younger than $\sim$1700 which yields a minimum sedimentation rate for the 38 cm core of 1.4 mm/yr, in good agreement with the range calculated above from chemical markers.

Such a sedimentation rate, obtained by using two well spaced chemical markers, which behave similarly in the sediments (PCB and hydrocarbons), agrees favorably to the sedimentation rate of 2.9 mm/yr established by ^{210}Pb geochronology on a Buzzards Bay core, some 40 km to the east of our sampling site (Farrington et al., 1977b).

The UCM does not disappear completely with age (depth) as natural pyrolytic sources (e.g. forest fires) (Youngblood and Blumer, 1976) probably contributed aromatic and naphthenic hydrocarbon compounds to the atmosphere and hence the sediments via fallout and runoff, long before the increased usage of petroleum began to dominate the sedimentary hydrocarbon

assemblage. We suggest that the recent sedimentary record in estuarine and coastal areas, on continental shelves and in freshwater bodies around and within industrialized regions, contains an accurate marker of increased UCM concentrations. This marker and those of individual compounds which may be chromatographically resolved using capillary columns (e.g. see Dastillung and Albrecht, 1975), could serve as useful chemical horizons in sediments where natural petroleum seepages have not occurred. Used in conjunction with another anthropogenic marker having a different depositional history (e.g. PCBs), these horizons could then be used to obtain a sedimentation rate of that sediment deposited subsequent to the input of anthropogenic hydrocarbons.

SECTION V

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